

High Tc Superconductivity in the Triple-Perovskite La-Rare Earth or Alkali Metal-Ba-Ca-Mg or Cd-Cu-Oxide System

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Bulk targets of compounds in the system La _{3-z} Me _z Ba ₃ Ca _{1-v} Nc _v Cu ₇ O _{16+v} where Me=rare earth or Na and Nc=Mg or Cd were prepared by solid state reactions. They were employed to deposit by pulse laser deposition thin films of the superconductor on single crystal substrates of LaA10 ₃ , LSAT, and GGG. Phase relationships and orientation relationships were obtained from diffractometer scans. All compounds exhibited a (002) relationship with all substrates. Lattice parameters, transition temperatures and widths are reported for each superconducting compound. All substituted compounds were superconducting but no increase in Tc was observed for any. All thin films heated to 750 deg C desorbed little oxygen compared to YBCO.								
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HIGH T_c SUPERCONDUCTIVITY IN THE TRIPLE-PEROVSKITE La-RARE EARTH OR ALKALI METAL-Ba-Ca-Mg OR Cd-Cu-Oxide SYSTEM

INTRODUCTION

The high T_c superconducting system $\text{La}_{3\text{-z}}\text{Me}_z\text{Ba}_3\text{Ca}_{1\text{-v}}\text{Nc}_v\text{Cu}_7\text{O}_{16+x}$ is attractive for device applications because it is stable with regard to oxygen compared to $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and undergoes no phase transition between the sintering temperature and room temperature [1]. Thermal cycling demonstrated reversible oxygen losses of less than 1% up to 1000 °C in bulk samples [2]. One useful consequence should be more easily prepared multilayered structures and such multilayered devices as Josephson junctions, broadband impedance transformers, and flux flow and field effect transistors. One objective of this investigation has been the preparation and characterization of thin films of $\text{La}_3\text{Ba}_3\text{Ca}\text{Cu}_7\text{O}_{16+x}$. A second objective has been an investigation of the effect of substitutions for La and Ca with the hope of increasing T_c .

A superconducting bulk compound in the system $\text{La}_{3-z}\text{Me}_z\text{Ba}_3\text{Ca}_{1-v}\text{Nc}_v\text{Cu}_7\text{O}_{16+x}$ where z=0 and v=0, namely $\text{La}_3\text{Ba}_3\text{Ca}\text{Cu}_7\text{O}_{16+x}$ (La3317), was first prepared by Engelsberg [3]. The material was found to be a superconductor with a T_c = 80.2 K and to have a triple perovskite structure. It is tetragonal with c=3a (c=11.61, a=3.87). In an earlier study [4], carried out on a composition close to La3317, it was deduced that most of the Ca atoms occupy the central position of the unit cell that is occupied by Y atoms in YBa $_2\text{Cu}_3\text{O}_{6+x}$ (YBCO). Recently Kao et al. [5] reported that about half of the Ca enter the Y sites and the remainder are on Ba sites. Similar results have been obtained in studies of other La-Ba-Ca-Cu-oxides [4,6] where much of the La is found on the Ba sites.

The substitution of Mg and Sc for Ca was already investigated by Engelsberg [3]. He found a slight increase in lattice parameter when Mg is substituted, $c=11.71\text{\AA}$ and $a=3.91\text{\AA}$; and superconductivity was observed below 30 K. Sc substitution led to a multiphase material and no superconductivity was observed. Wu et al. [7] have investigated rare earth substitution for La in bulk samples.

EXPERIMENT

Bulk samples and targets, in the system $\text{La}_{3-2}\text{Me}_z\text{Ba}_3\text{Ca}_{1-v}\text{Nc}_v\text{Cu}_7\text{O}_{16+x}$ where Me=Nd, Yb, Y and Nc=Mg or Cd, were prepared for pulsed laser deposition (PLD) by mixing precursor powders of La_2O_3 , Nd_2O_3 , Yb_2O_3 , $\text{Y2}_2\text{O}_3$, Na_2CO_3 , MgO, and CdCO3 in a BC mortar until homogeneous. The powder was pressed into 2.54 cm discs and heated in air at 3 °C/min to 975 °C and held for 10 hours, cooled at 3 °C/min and removed from the furnace. Subsequently, the disc was reground to a powder of <100 μ m particle size and pressed into 2.54 cm diameter discs and re-pressed isostatically at 344 MPa. The discs were then heated at 3 °C/min to 1000 °C, held for 24 hours, in flowing oxygen gas. Lattice parameters were obtained from powder diffractometer scans taken between 15-155° 2θ using CuKα radiation (λ =1.54056 Å). Lattice parameters are reported in Table 1. Thin films prepared by PLD averaged about 300 nm thick. The observed reflections from films obtained by θ -2θ scans are reported in Table 1. Deposition parameters are as follows: KrF excimer laser (λ =248 nm) was used at a pulse repetition rate of 10 Hz and a laser fluence of 1-2 J/cm² at the target. The chamber was maintained at an oxygen pressure of 13.6 Pa and the heater block holding the substrates was held at 850 °C. Deposition times were about 10 minutes. Samples were cooled rapidly to 650 °C and then to 400°C in 5.17 kP of oxygen in 1/2 hr. The substrates employed in this investigation were single

crystal (211) GGG, (100) LaAlO₃, and (100) LSAT (a solid solution of 30 mole % LaAlO₃-70 mole % Sr₂AlTaO₆) [8,9]. The superconducting transition temperature and transition width were measured using an ac Eddy current apparatus. Bulk or thin film samples were mounted on a sapphire block in which a detecting pick up coil has been imbedded. The sample is mounted on the sapphire block above the detecting coil. An exciting coil driven at 100 MHz is placed above the sample. The sapphire block is in contact with the thermal sink of a closed cycle helium cryostat.

TABLE 1. Properties of $La_{3-z}Me_zBa_3Ca_{1-v}Cu_7O_{16+x}$ Compounds.

Compound	Lattice Parameter (Å)		Onset	ΔT_{c}	Observed	
	С	а	$T_{c}(K)$	(K)	Reflections	
La ₃ Ba ₃ CaCu ₇ O _{16+x}	11.650 11.680*	3.865	72 80*	4		
La ₃ Ba ₃ CaCu ₇ O _{16+x} /LSAT	11.665				003,005,006,007,0012	
La ₃ Ba ₃ CaCu ₇ O _{16+x} /GGG	11.540				003,005,006,007,009	
La ₃ Ba ₃ CaCu ₇ O _{16+x} /LaAlO ₃	11.660		35	15	003,004,005,006,007, 009,0011,0012	
La ₂ YBa ₃ CaCu ₇ O _{16+x}	11.580	3.850	72	3		
LaY ₂ Ba ₃ CaCu ₇ O _{16+x}	11.630	3.868	74	6		
LaY ₂ Ba ₃ CaCu ₇ O _{16+x} /LSAT	11.703	J			002,005,006,007	
Nd ₃ Ba ₃ CaCu ₇ O _{16+x}	11.614	3.874	42			
Nd ₃ Ba ₃ CaCu ₇ O _{16+x} /LSAT			40	20		
La ₂ YbBa ₃ CaCu ₇ O _{16+x}	11.530	3.843	74	5		
La ₂ YbBa ₃ CaCu ₇ O _{16+x} /LSAT	11.628		45	>20	003,005,006,007, 009,0010,0011	
La ₂ YbBa ₃ CaCu ₇ O _{16+x} /LaAlO ₃	11.630				003,005,006,007,008, 009,0010,0011	
La ₂ YbBa ₃ CaCu ₇ O _{16+x} /GGG	11.683				003,005,006,007	
La _{2.5} Na _{.5} Ba ₃ CaCu ₇ O _{16+x}	11.630	3.870	68	18	[multiphase]	
La _{2.5} Na _{.5} Ba ₃ CaCu ₇ O _{16+x} /LaAlO ₃	11.662		65	>40	003,005,006,007	
La _{2.5} Na _{.5} Ba ₃ CaCu ₇ O _{16+x} /GGG	11.664				006,009	
La ₃ Ba ₃ Ca _{.5} Cd _{.5} Cu ₇ O _{16+x}	11.661	3.881	55			
$La_3Ba_3Ca_5Cd_5Cu_7O_{16+x}/LSAT$	11.720				003,006	
$\text{La}_{3}\text{Ba}_{3}\text{Ca}_{.5}\text{Cd}_{.5}\text{Cu}_{7}\text{O}_{16+x}/\text{LaAlO}_{3}$	11.265		70	>45	003,006	
La ₃ Ba ₃ Ca _{.5} Cd _{.5} Cu ₇ O _{16+x} /GGG	11.730				003,006,007	
$\text{La}_{3}\text{Ba}_{3}\text{Ca}_{.5}\text{Mg}_{.5}\text{Cu}_{7}\text{O}_{16+x}$	11.661	3.890	35	15		
La ₃ Ba ₃ Ca _{.5} Mg _{.5} Cu ₇ O _{16+x} /LaAlO ₃	11.650				003,005,006,007, 009,0010,0011	
La ₃ Ba ₃ Ca _{.5} Mg _{.5} Cu ₇ O _{16+x} /GGG	11.692				003,005,006,007,0011	

^{*}Reference [3].

Desorption of oxygen from several films was investigated as a function of temperature using thermal desorption mass spectrometry. This involves detecting desorbing O2 using a double focusing mass spectrometer. The spectrometer has high mass resolution which allows the oxygen signal to be separated from other interfering species such as hydrocarbons of the same nominal mass (i.e., 32 AMU). For analysis, a piece of a thin film coated substrate was introduced into a tantalum foil cell. Spotwelded to the cell was a 0.005 in. 5%Re-W/26%Re-W thermocouple. The cell was attached to a vacuum feedthrough that allowed samples to be moved into a roughing chamber and then into an analysis chamber containing the mass spectrometer. The base pressure of the analysis chamber at the onset of the desorption was in the mid 10-9 Torr range. This provided a low oxygen background and an increased sensitivity for detecting oxygen originating from the contents of the cell. The cell temperature could be ramped to 1500 °C, but typically a maximum of 800 °C was used. A linear temperature ramp of 1.4 K/sec was maintained using a feedback temperature controller and a 100 amp power supply. The area of the film was determined by computer processing a scanned image of the sample. The sample thickness was determined by fracturing a coated substrate and measuring the film cross section using scanning electron microscopy. oxygen desorption spectra were then normalized to the calculated volume of the film for each sample respectively.

RESULTS

All substitutions for either La or Ca resulted in the preservation of the tetragonal structure. In bulk samples, changes in intensity of x-ray diffraction lines are consistent with the increase or decrease in the scattering power of the substituent. Very small changes in the c lattice parameter are also noted, consistent with the changes in ionic radii of substituent ions, while the a parameter exhibited a slight expansion. For thin films, contractions in the c parameter were observed when the substrate was LaAlO₃; slight expansion was found when LSAT or GGG substrates were used. The results of lattice expansion or contraction of the film are consistent with known lattice parameters for the substrates. All films showed the same epitaxial relationship regardless of substrate: La_{3-z}Me_zBa₃Ca_{1-v}Nc_vCu₇O_{16+x} (00\$\mathref{x}\$) on (100)LaAlO₃, on (100)LSAT or on (211) GGG, Table 1. The strongest reflection from each of these films was always (006). The best quality films obtained, as judged by the presence of higher order reflections, were those deposited on LaAlO₃. This may be due to the fact that of all the substrates employed, only LaAlO₃ placed the films in compression, or film deposition conditions were not optimized.

CONCLUSIONS

All substituent compounds exhibited high T_c superconductivity, although the transition temperatures were lower than in the unsubstituted compounds. The highest transition temperatures were obtained when rare earth ions replaced La. Engelsberg found that the substitution of Mg for Ca resulted in a reduced T_c [3]. We observed a T_c =35 K upon the replacement of half of the Ca by Mg; this was close to what Engelsberg observed. On the other hand, the substitution of half the Ca by Cd in this investigation resulted in a much higher transition temperature, 55 K. The fact that divalent Cd is much larger than Mg and has an ionic radius close to Ca suggests that ionic size might be a major factor influencing superconductivity. However, the nature of the bonding is probably a major factor as well.

All the thin film compounds prepared in this investigation desorb very little oxygen when heated compared with YBCO, Fig. 1(A). When some La is replaced by Na the largest desorption for any substituted compound was observed, Fig. 1(C). The substitution of Cd for Ca has a smaller effect, Fig. 1(E). It appears that occupancy by light rare earths (large ionic radii), in the rare earth site for this triple perovskite structure, strongly influences the retention of oxygen with heating.

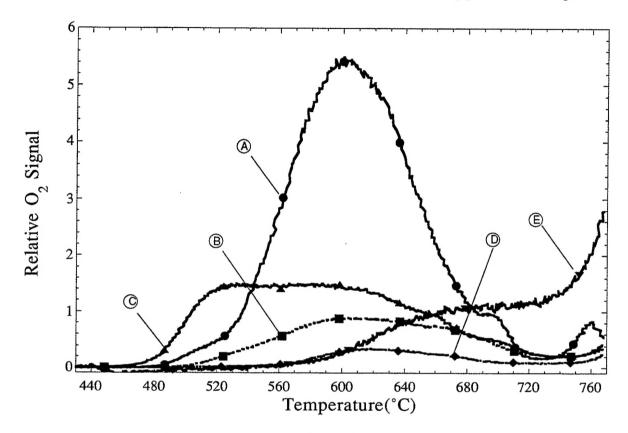


Figure 1. Desorption of oxygen from thin films: (A) $YBa_2Cu_3O_{6+x}$, (B) $Nd_3Ba_3CaCu_7O_{16+x}$, (C) $La_{2.5}Na_{.5}Ba_3CaCu_7O_{16+x}$, (D) $La_3Ba_3CaCu_7O_{16+x}$ and (E) $La_3Ba_3Ca_{.5}Cd_{.5}O_{16+x}$.

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